MRCI study of spectroscopic and molecular properties of $X^1\Sigma_g^+$ and $A^1\Pi_u$ electronic states of the C_2 radical*

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The potential energy curves (PECs) of $X^1\Sigma_g^+$ and $A^1\Pi_u$ electronic states of the C_2 radical have been studied using the full valence complete active space self-consistent field (CASSCF) method followed by the highly accurate valence internally contracted multireference configuration interaction (MRCI) approach in conjunction with the aug-cc-pV6Z basis set for internuclear separations from 0.08 nm to 1.66 nm. With these PECs of the C_2 radical, the spectroscopic parameters of three isotopologues ($^{12}C_2$, $^{12}C^{13}C$ and $^{13}C_2$) have been determined. Compared in detail with previous studies reported in the literature, excellent agreement has been found. The complete vibrational levels $G(v)$, inertial rotation constants B_v and centrifugal distortion constants D_v for the $^{12}C_2$, $^{12}C^{13}C$ and $^{13}C_2$ isotopologues have been calculated for the first time for the $X^1\Sigma_g^+$ and $A^1\Pi_u$ electronic states when the rotational quantum number J equals zero. The results are in excellent agreement with previous experimental data in the literature, which shows that the presented molecular constants in this paper are reliable and accurate.

Keywords: potential energy curve, spectroscopic parameter, molecular constant, isotope effect

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1. Introduction

C_2 is one of the fundamental radicals that are of interest in many disciplines. It is abundant in flames, combustion sources, explosions and hydrocarbon discharges.[1,2] It has been observed in many extraterrestrial sources, such as comets, carbon stars, protoplanetary nebulae and molecular clouds.[3,4] Due to its simplicity, the ground and lowest single electronic states, $X^1\Sigma_g^+$ and $A^1\Pi_u$, have been widely studied, both experimentally and theoretically.

The $A^1\Pi_u$–$X^1\Sigma_g^+$ electronic transition of the C_2 radical was observed by Phillip[5] experimentally as early as 1948. Since then, a number of investigations[6−16] have been made of the two electronic states. In theory, a host of *ab initio* calculations have been done, and the vibrational frequency, dissociation energy, equilibrium internuclear separation and other spectroscopic parameters have been determined.[2,17−43] However, little information has been reported on the molecular properties, such as vibrational manifolds, especially for the $^{12}C^{13}C$ and $^{13}C_2$ isotopologues. Thus, to understand the spectroscopic and molecular properties of these isotopologues more completely, more detailed high-level calculations are still needed.

The natural abundances of ^{12}C and ^{13}C are about 98.93% and 1.07%, respectively. ^{14}C is neglected in the present calculations because of its low natural abundance. Hence, we only study the properties of the three main isotopologues, i.e., $^{12}C_2$, $^{12}C^{13}C$ and $^{13}C_2$. For these isotopologues, their natural abundances are about 97.872% ($^{12}C_2$), 2.117% ($^{12}C^{13}C$) and 0.011% ($^{13}C_2$), respectively.

This paper is organized as follows. First, the potential energy curves (PECs) of $X^1\Sigma_g^+$ and $A^1\Pi_u$ electronic states of the C_2 are calculated over the internuclear separation from 0.08 nm to 1.66 nm using the full valence complete active space self-consistent field (CASSCF) method followed by the highly accurate valence internally contracted multireference configuration interaction (MRCI) approach[44,45] in combination with the aug-cc-pV6Z correlation-consistent basis set.[46] Then, with these PECs of the C_2 radical, the spectroscopic parameters of the $^{12}C_2$, $^{12}C^{13}C$ and $^{13}C_2$ isotopologues are obtained. Finally, the vibrational manifolds (such as vibrational levels, inertial rotation and centrifugal distortion constants) are determined for the first 20 vibrational levels for the two electronic states when the rotational quantum number J equals zero. Comparison with the available exper-

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imental data in the literature shows that our results are more accurate than those obtained by previous theoretical calculations on the whole.

2. Calculation details

The PECs of $X^1\Sigma_g^+$ and $A^1\Pi_u$ electronic states were computed by the CASSCF and subsequent MRCI approach. Therefore, the full valence CASSCF is used as the reference wavefunction for the MRCI calculations. For the PEC calculations of diatomic molecules,[47−51] the MRCI theory has been proven to be successful in particular. All of the PEC calculations were carried out with the MOLPRO 2008.1 program package[52] for internuclear separations from 0.08 nm to 1.66 nm. The basis set used here is aug-cc-pV6Z in the valence range.

MOLPRO only uses Abelian point group symmetry. That is, for diatomic molecules such as C_2 with $D_{\infty h}$ symmetry, $a_g/b_{3u}/b_{2u}/b_{1g}/b_{1u}/b_{2g}/b_{3g}/a_u$ irreducible representations of D_{2h} group are used. In the CASSCF and subsequent MRCI calculations, these eight kinds of states need to be considered. In detail, for the C_2 radical, eight molecular orbitals (MOs) are put in the active space, including two a_gs, one b_{3u}, one b_{2u}, two b_{1u}s, one b_{2g} and one b_{3g} symmetry MOs, which correspond to the 2s2p shell of the C atom. The rest of the electrons in the C_2 radical are put into two closed-shell core orbitals, including only one a_g and one b_{1u} symmetry MOs. For the $A^1\Pi_u$ electronic state, these MOs (three a_gs, one b_{3u}, one b_{2u}, three b_{1u}s, one b_{2g} and one b_{3g}) are used to carry out the PEC calculations, and we find that the PEC is smooth over the present internuclear distance range. For the $X^1\Sigma_g^+$ electronic state, however, there is a bump in the PEC under the same condition. Detailed analysis shows that this situation is caused by PEC crossing. In order to improve the smoothness of the PEC, more MOs are put into the active space, including an additional a_g and an extra b_{3u} MOs. Using these MOs (four A_gs, two B_{1g}s, one b_{2u}, three b_{1u}s, one b_{2g} and one b_{3g}), the $C_2(X^1\Sigma_g^+)$ PEC obtained is both smooth and convergent over the present internuclear separation range.

The PEC calculations were performed with an interval of 0.02 nm for internuclear distances from about 0.08 nm to 1.66 nm. Only near the equilibrium position the interval is 0.005 nm. The smaller step adopted around the equilibrium position of each electronic state makes the properties of each PEC display clearer.

With the PECs obtained at the MRCI/aug-cc-pV6Z level of theory, the spectroscopic parameters and molecular constants for the $X^1\Sigma_g^+$ and $A^1\Pi_u$ electronic states of three isotopologues ($^{12}C_2$, $^{12}C^{13}C$ and $^{13}C_2$) are evaluated with the aid of the VIBROT module in the MOLCAS 7.4 program package.[53] In the VIBROT module, the potential is fitted to an analytical form using cubic splines. The ro-vibrational Schrödinger equation is then solved by Numerov's method[54] for one vibrational level at a time and for a number of rotational quantum numbers, as specified by the input. And the spectroscopic parameters are determined by fitting the vibrational levels. Here, the spectroscopic parameters for the $^{12}C_2$ species are given in Table 1 and those for the $^{12}C^{13}C$ and $^{13}C_2$ isotopologues are shown in Table 2. For convenient comparison, those results collected from the literature[2,6−43] are also listed in Table 1.

Table 1. Spectroscopic parameters for $^{12}C_2$ species.

source	D_e/eV	R_e/nm	ω_e/cm^{-1}	$\omega_e x_e$/cm^{-1}	$10^6 D_{rot}$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	D_0/eV
$X^1\Sigma_g^+$								
this work	6.3185	0.12454	1853.53	12.755	6.8781	1.8113	0.0174	6.2040
exp.[6]	–	–	–	–	–	–	–	6.25(0.20)
exp.[9]	–	–	1854.783	13.389	6.9590	1.8200	0.01768	–
exp.[10]	6.3246	0.12425	1854.71	13.340	6.92	1.8198	0.0176	6.21
exp.[13]	–	–	1854.588	13.273	6.9393	1.8199	0.01775	–
exp.[14]	–	0.12424	1855.014	13.555	6.9640	1.8201	0.0180	–
exp.[16]	–	0.12419	1855.066	13.601	6.9526	1.8201	0.0179	–
theory[2]								
CASSCF	6.06	0.1252	1835.5	14.9	–	1.792	0.0157	5.95
CCI	5.94	0.1246	1870.6	15.8	–	1.809	0.0155	5.82
theory[17]	5.39	0.13559	1503	–	–	–	–	–
theory[18]	6.29	0.1242	1864	–	–	–	–	–

Table 1. (*Continued*)

source	D_e/eV	R_e/nm	ω_e/cm^{-1}	$\omega_e x_e$/cm^{-1}	$10^6 D_{rot}$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	D_0/eV
theory[19]	6.310	0.12457	1854	–	–	–	–	6.195
theory[20]	6.1230	0.12458	1857	–	–	–	–	–
theory[21]	6.41	0.1244	1850	–	–	–	–	–
theory[22]	6.3124	0.12448	1832	[MR-CISD+Q/CBS/TQ]				
	6.2777	0.12453	1847	[MR-CISD/CBS/TQ]				
	6.2959	0.12452	1842	[MR-AQCC/CBS/TQ]				
theory[23]	–	0.12647	–	–	–	–	–	–
theory[24]	–	0.1255	1970	–	–	–	–	–
theory[25]	–	0.1248	1803	–	–	–	–	–
theory[26]								
SCF	0.79	0.1239	–	–	–	–	–	–
SDCI	4.27	0.1240	–	–	–	–	–	–
theory[27]	–	0.12786	–	–	–	–	–	6.92
theory[28]	6.3149	0.12459	[MRCI(Q)/CBS/AVXZ]					
	6.3968	0.12424	[MRCI(Q)/CBS/ACVXZ]					
theory[29]	6.3984	0.12424	–	–	–	–	–	–
theory[30]	5.55	0.126	1788.6	13.6	–	1.76	0.018	–
theory[31]	6.25	0.12393	1897	12.85	–	1.829	0.0171	–
theory[32]	–	0.12494	1860	–	–	1.80	–	–
theory[33]	–	0.12462	1835.0	15.5	–	1.81	0.019	–
theory[34]	6.2921	0.12459	1854.4	12.7	–	1.810	0.0173	–
theory[35]	6.2245	0.12465	1848.2	12.9	–	1.808	0.0175	–
theory[36]	5.8662	0.1252	1852	13	–	–	0.018	–
theory[37]	–	0.12467	1852.8	–	–	1.8059	–	6.18
theory[38]	6.1057	0.12455	1858	12.6	–	–	–	–
theory[39]	6.6418	0.12594	1834.785	12.405	–	1.7571	0.01515	–
theory[40]	5.6677	0.12539	1837	11.41	–	1.8254	0.0166	–
theory[41]	5.99	0.12596	1859	13.2	6.43	1.771	0.017	–
theory[42]	6.99	0.1241	1864	13.4	–	1.824	0.0177	–
theory[43]	5.88	0.12586	1833.66	13.46	–	1.7608	–	–
$A^1\Pi_u$								
this work	5.2352	0.13225	1598.87	12.026	6.4628	1.6062	0.01681	5.1365
exp.[9]	5.2842	–	1608.22	12.055	6.4944	1.6165	0.01687	–
exp.[10]	5.2842	0.13184	1608.35	12.07	6.44	1.6163	0.01686	–
exp.[13]	5.2842	–	1608.31	12.128	6.4875	1.6165	0.01692	–
exp.[14]	5.2842	0.13183	1608.199	12.060	6.5086	1.6166	0.01697	–
exp.[16]	5.2842	0.13177	1608.232	12.085	6.5005	1.6166	0.01695	–
theory[17]	3.91	0.13925	1527	–	–	–	–	–
theory[22]	5.3312	0.13321	1595	[MR-CISD+Q/CBS/TQ]				
	5.2402	0.13214	1597	[MR-CISD/CBS/TQ]				
	5.2945	0.13213	1596	[MR-AQCC/CBS/TQ]				
theory[24]	–	0.1306	1730	–	–	–	–	–
theory[26]								
SCF	–	0.1288	–	–	–	–	–	–
SDCI	–	0.1307	–	–	–	–	–	–
theory[30]	4.41	0.134	1507.5	5.0	–	1.55	0.016	–
theory[32]	–	0.13330	1548	–	–	1.58	–	–
theory[33]	–	0.13208	1615.0	10.6	–	1.61	0.018	–
theory[36]	4.8505	0.1317	1592	13	–	–	0.018	–
theory[37]	–	0.1323	1596.1	–	–	1.6040	–	5.12
theory[40]	–	0.13220	1610	10.28	6.40	1.6077	0.0160	–

Note: data in this work were obtained at the MRCI/aug-cc-pV6Z level of theory.

Table 2. Spectroscopic parameters for the $^{12}C^{13}C$ and $^{13}C_2$ isotopologues at the MRCI /aug-cc-pV6Z level of theory compared with available experimental data.

source	D_e/eV	R_e/nm	ω_e/cm^{-1}	$\omega_e x_e$/cm^{-1}	$D_{rot}(\times10^{-6})$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	D_0/eV
$^{12}C^{13}C(X^1\Sigma_g^+)$								
this work	6.3185	0.12454	1817.27	12.105	6.4140	1.7415	0.0164	6.2062
exp.[12]	–	–	1818.651	12.872	6.4320	1.7498	0.0167	–
$^{13}C_2(X^1\Sigma_g^+)$								
this work	6.3185	0.12454	1780.43	11.614	6.0126	1.6716	0.0155	6.2085
exp.[12]	–	–	1781.788	12.356	5.9265	1.6796	0.0158	–
$^{12}C^{13}C(A^1\Pi_u)$								
this work	5.2352	0.13225	1567.73	11.645	5.8911	1.5443	0.0154	5.1384
$^{13}C_2(A^1\Pi_u)$								
this work	5.2352	0.13225	1535.95	11.182	5.5275	1.4823	0.0149	5.1404

In order to evaluate the effect of the core-valence correlation correction on the spectroscopic parameters, we calculated the PECs of the two electronic states using the aug-cc-pCV5Z basis set over a small internuclear separation range near the equilibrium position. For comparison, the spectroscopic parameter calculations were also carried out using the PECs obtained from the aug-cc-pCV5Z basis set[55] with the aid of the VIBROT module presented in the MOLCAS 7.4 program package.[53] By comparison with the experimental data,[6,9,10,13,14,16] we find that the spectroscopic parameters obtained from the aug-cc-pCV5Z basis set improve little compared with the proposed ones. Because the PEC calculations from the aug-cc-pCV5Z basis set over a wide internuclear separation range consume more CPU processing time, we only use the PECs obtained from the aug-cc-pV6Z basis set for further vibrational manifold investigations.

3. Results and discussion

3.1. Spectroscopic parameters

For convenient comparison, we collect the spectroscopic parameters obtained by this work, from literature including experimental data[6,9,10,13,14,16] and theoretical calculations[2,17−43] for $^{12}C_2$ in Table 1 and for $^{12}C^{13}C$ and $^{13}C_2$ in Table 2.

With respect to the spectroscopic parameters of the C_2 radical, early theoretical results were reported by Fougere *et al.*[17] in 1966, who carried out the calculations of spectroscopic properties for the 27 electronic states for internuclear separations from 1.5 a_0 to 8.0 a_0 employing two different configuration interaction (CI) approaches, together with three different Slater-type-orbital (STO) basis sets. In these investigations, the spectroscopic parameters were fitted by the interpolation procedure. By comparing with the experiments,[6,9,10,13,14,16] we find that in their results the closest to the experimental data were determined by the semi-PAN approach with the 6XB+D STO basis set. As listed in Table 1, their D_e and ω_e values are far from the experimental data.[10] Similar to Ref. [17], there are five theoretical studies,[18−22] in which only the D_e, R_e and ω_e were determined. For example, Watts *et al.*[18] in 1992 carried out the coupled-cluster calculations on the ground and some excited electronic states of C_2 using several basis sets. Among their results, the closest to the experimental data were determined by the cc-pVQZ basis set. Sordo[20] in 2001 carried out the CCSDT/aug-cc-pVnZ (n = D, T, Q) calculations on several diatomic molecules and their ions. Here we select the results obtained from the aug-cc-pVQZ basis set for comparison. Müller *et al.*[22] in the same year made systematic theoretical investigations for the valence excited states of several diatomic molecules. In those calculations, three kinds of methods were applied, which were multireference CI with all singles and doubles (MR-CISD), MR-CISD with the Davidson correction (MR-CISD+Q) and multireference averaged quadratic coupled cluster (MR-AQCC). The basis sets they used were the cc-pVTZ and cc-pVQZ. For the C_2 radical, as listed in Table 1, their D_e and ω_e results[18−22] are all inferior to ours.

Langhoff *et al.*[23] in 1977 reported R_e value at several theoretical levels. By comparison with the available experimental data in the literature, their favorable spectroscopic results were obtained by the extensive CI approach with a double-zeta basis of

Gaussian-lobe functions and including $d\sigma$ and $d\pi$ functions. The deviation in their R_e, 0.12647 nm, from the experimental data[10] is 2.22%, whereas the deviation in the present work is only 0.23%.

Two theoretical studies,[24,25] only determining the R_e and ω_e, were made by Verhaegen *et al.*[24] in 1967 and Bauschlicher *et al.*[25] in 1987. Verhaegen *et al.*[24] performed the PEC calculations on three different configurations for the C_2 by the linear combination of atomic orbitals (LCAO) MO SCF method. Comparing with the experimental data,[10] we find that their ω_e values for the two electronic states are inferior to oors. Bauschlicher *et al.*[25] carried out the full CI (FCI) and CASSCF/MRCI calculations on the C_2 using the valence double-zeta plus polarization one-particle basis set. By comparing their results with the experimental data, we find that the CASSCF/MRCI method is superior to the FCI in obtaining the spectroscopic properties of low-lying electronic states. However, the ω_e values are still far from the experimental data.[10]

Four studies[26−29] only determined the D_e and R_e values. Mclean *et al.*[26] in 1992 performed the PEC calculations using the SCF and singles and doubles CI (SDCI) approaches for several molecules. The spectroscopic parameters of four electronic states of C_2 were obtained. Their D_e value of the ground state and R_e value of the $A^1\Pi_u$ electronic state obviously deviate from the experimental data.[10] Valdes *et al.*[27] in 1997 used the density functional theory to determine the structural parameters and energies for the C_{1-3} and C_9 clusters. Their R_e and D values are far from the experimental data.[9,10] Varandas[28] in 2008 studied the C_2 bond breaking of $X^1\Sigma_g^+$, $B^1\Delta_g$ and $B'^1\Sigma_g^+$ electronic states using the MRCI method including Davidson correction for quadruple excitations [MRCI(Q)] in conjunction with the correlation-consistent basis sets. At the complete basis set (CBS) limit of aug-cc-pCVnZ basis sets, their D_e and R_e are 6.3968 eV and 0.12424 nm, respectively. Their R_e values agree favorably with the experimental data, while their D_e greatly deviate from the measurements.[10] At the CBS limit of aug-cc-pVnZ basis sets, for the $X^1\Sigma_g^+$ electronic states, their D_e and R_e are 6.3149 eV and 0.12459 nm, respectively, and these results are still inferior to the present ones. Varandas[29] in 2009 reported a scheme for the direct diabatization of two adiabatic states showing an avoided intersection. All of their calculations were performed with the CASSCF followed by the MRCI utilizing AVXZ and ACVXZ basis sets. The results listed in Table 1 are obtained at the CBS limit of ACVXZ basis sets. As listed in Table 1, their D_e value is a little larger than ours compared with the available measurements.[10]

Most theoretical studies[2,30−43] involved the spectroscopic parameters $\omega_e x_e$, α_e and B_e. Kirby *et al.*[30] in 1979 computed the PECs of 62 valence states by the CI method and the STF basis set. Using these PECs, they evaluated the spectroscopic parameters of 19 electronic states of C_2 by cubic spline fits. Obviously, their results are far different from the experimental data.[6,9,10,13,14,16] Dupuis *et al.*[31] in 1980 calculated the $C_2(X^1\Sigma_g^+)$ PEC using the SCF, MCSCF and CI approaches. Favorite spectroscopic constants were obtained by the CI calculations, including all single and double excitations from the restricted Hartree–Fock configuration with corrections for the quadrupole excitation estimated by a formula due to Davidson correction. Their R_e and B_e agree well with the measurements, whereas the D_e, ω_e, $\omega_e x_e$ and α_e are much poorer than those in the present work. Chabalowski *et al.*[32] in 1983 emphasized the computation of intensity distributions (lifetimes) associated with Ballik–Ramsay ($b^3\Sigma_g$–$a^3\Pi_u$), Mulliken ($D^1\Sigma_u^+$–$X^1\Sigma_g^+$) Deslandres-d Azambuja ($C^1\Pi_g$–$A^1\Pi_u$) and Phillips ($A^1\Pi_u$–$X^1\Sigma_g^+$) systems. However, their R_e ω_e and B_e values for these two electronic states are still inferior to the ones in the present work compared with the experimental data.

Kraemer *et al.*[2] in 1987 performed the PEC calculations of the $X^1\Sigma_g^+$ and $a^3\Pi_u$ electronic states of C_2 radical. Their calculations were carried out at the CASSCF and multireference contracted CI (CCI) levels with a large Gaussian basis set augmented by the three d-type polarization functions. Spectroscopic parameters obtained by the two methods are inferior to the ones proposed here. Bruna *et al.*[33] in 1992 reported the theoretical study of the transition probabilities of several electronic states of C_2 using MRD-CI wavefunction. By fitting, they obtained several spectroscopic parameters of some electronic states. However, their $\omega_e x_e$ are obviously far different from the experimental ones.[10] Peterson *et al.*[34] in 1993 made the ground-state PEC calculations of B_2, C_2, N_2, O_2 and F_2 by several methods (such as SD-CI, HF+1+2, GVB+1+2 and CAS+1+2) with correlation-consistent basis sets from double through quintuple zeta quality. Using the PECs, they fitted several spectroscopic parameters. The results obtained at the CASSCF+1+2/cc-pV5Z level of theory are found to be in line with the RKR data. Although their R_e value agrees favourably with the available

measurements, other spectroscopic parameters are inferior to those presented here. Peterson[35] in 1995 performed the large internally contracted multireference CI (CMRCI) calculations on the $1^1\Sigma_g^+$ and $1^3\Pi$ electronic states of C_2, CN^+, BN, and BO^+. As shown in Table 1, the D_e value is still a little smaller than ours.

Sorensen *et al.*[36] in 1998 calculated the total-energy curves for several valence states of C_2 using Feynman's method. In their calculations, the basis set used was an even-tempered correlation-consistent (10s5p2d1f)/[4s3p2d1f] generally contracted (s and p sets augmented with most diffuse primitives) Gaussian basis set. By fitting, they determined several spectroscopic parameters (D_e, R_e, ω_e, $\omega_e x_e$ and α_e) of a number of electronic states. As for the involved states $X^1\Sigma_g^+$ and $A^1\Pi_u$, we find that their D_e and R_e are much different from the available experimental results[10] compared with ours. Boggio-Pasqua *et al.*[37] in 2000 calculated the PECs of 12 electronic states for internuclear separations from 1.8 a_0 to 20 a_0 with the CMRCI theory and the cc-pV5Z basis set. They obtained the analytical representations of PECs and determined the spectroscopic parameters (R_e, ω_e, B_e and D) of the C_2. As listed in Table 1, one can see that few spectroscopic parameters are superior to the proposed ones, in particular for D_0. Feller *et al.*[38] in the same year performed a series of CCSDT calculations with the cc-pVDZ, cc-pVTZ and cc-pVQZ basis sets for the ground state of the first and second row diatomic molecules. Here, the results under the CCSDT/cc-pVQZ theory are chosen for comparison. Deviations in their D_e from the measurements are somewhat large. Wang *et al.*[39] in 2001 made the PEC calculations for the ground state of C_2 radical by the QCISD/6-311G* level of theory. Their results are also far different from the experimental results.[10] Meißner *et al.*[40] in 2001 used the direct generalized Bloch (DGB) approach with different basis sets to calculate the PECs of the $X^1\Sigma_g^+$, $a^3\Pi_u$, $b^3\Sigma_g$ and $A^1\Pi_u$ electronic states. Close agreement with the experimental data is achieved by the BQ2 approximation with the s-pVTZc basis set. Their B_e is in excellent agreement with the available measurements,[9,10,13,14,16] while the values of D_e, $\omega_e x_e$ and α_e are much poorer than the ones in this work

Abrams *et al.*[41] in 2003 carried out FCI benchmark computations with the 6-31G**, DZP, cc-pVDZ and atomic natural orbital (ANO) basis sets. Several spectroscopic parameters of the $C_2(X^1\Sigma_g^+)$ were determined. The results obtained by the FCI/6-31G** method are found to be the closest to the experimental ones.[10] Their spectroscopic parameters except for $\omega_e x_e$ are inferior to ours. Kamiya *et al.*[42] in 2007 calculated the spectroscopic parameters of C_2 using the high-order equation-of-motion coupled-cluster methods for electron attachment (EA-EOM-CC) approach. Their results obtained by the CCSDTQ/CBS+Δ_{core} method agree well with the experimental findings[6,9,10,13,14,16] except for D_e. Mahapatra *et al.*[43] in 2008 calculated the PEC of the $C_2(X^1\Sigma_g^+)$ using the size-extensive state-specific multireference perturbation theory (SS-MRPT) in combination with several basis sets. By fitting, they determined several spectroscopic parameters. As listed in Table 1, their D_e, R_e and ω_e results are still far different from the experimental ones.[10]

As discussed above, for the $^{12}C_2$ species, we say that the results presented here are more accurate and complete than those obtained in previous theoretical investigations. For example, the spectroscopic parameters in this work deviate from the experiments[10] only by 0.10% (D_e), 0.23% (R_e), 0.07% (ω_e), 4.39% ($\omega_e x_e$), 0.61% (D_{rot}), 0.47% (B_e) and 0.14% (α_e) for the $X^1\Sigma_g^+$ electronic state and 0.93%, 0.31%, 0.59%, 0.36%, 0.35%, 0.62%, 0.30%, for the $A^1\Pi_u$ electronic state. Therefore, we can conclude that the spectroscopic parameters achieved by this work are much high accuracy.

To the best of our knowledge, only one study[12] reported the ground-state spectroscopic parameters of $^{12}C^{13}C$ and $^{13}C_2$ isotopologues. For the $^{12}C^{13}C(X^1\Sigma_g^+)$ species, the deviations of the present ω_e, $\omega_e x_e$, D_{rot}, B_e and α_e from the experimental data[12] are 0.08%, 5.96%, 0.28%, 0.47% and 1.80%, respectively; and for the $^{13}C_2(X^1\Sigma_g^+)$ species, such deviations are only 0.08%, 6.01%, 1.45%, 0.48% and 1.90%, respectively. Hence, we could conclude that the ground-state spectroscopic parameters of $^{12}C^{13}C$ and $^{13}C_2$ isotopologues are very reliable.

However, for the $A^1\Pi_u$ electronic state, no spectroscopic results can be found in the literature for the $^{12}C^{13}C$ and $^{13}C_2$ isotopologues. As discussed above, for a given electronic state, the spectroscopic parameters of $^{12}C_2$, $^{12}C^{13}C$ and $^{13}C_2$ isotopologues are determined by the same PEC and fitting method. Because the spectroscopic parameters of the $^{12}C_2$ are accurate, we can deduce that the spectroscopic parameters of $^{12}C^{13}C$ and $^{13}C_2$ isotopologues given in Table 2 for the $A^1\Pi_u$ electronic state are also accurate.

3.2. Vibrational manifolds

Using the PECs obtained at the MRCI/aug-cc-pV6Z level of theory, with the aid of the VIBROT module in the MOLCAS 7.4 program package,[53] we have determined the complete vibrational level $G(\upsilon)$, inertial rotation constant B_υ and centrifugal distortion constant D_υ for the $X^1\Sigma_g^+$ and $A^1\Pi_u$ electronic states of $^{12}C_2$, $^{12}C^{13}C$ and $^{13}C_2$ isotopologues. The present results of $G(\upsilon)$, B_υ and D_υ are shown in Tables 3–6, respectively. Due to the page limitation, we tabulate them here only for the first 20 vibrational levels. Again, the available experimental data[7,8,11,14] are listed for convenient comparison.

Two studies[7,14] reported the experimental $G(\upsilon)$ results for the $^{12}C_2(X^1\Sigma_g^+)$ species. Table 3 shows that a perfect agreement exists between the present results and the experimental ones.[7,14] For example, the largest deviation in the present $G(\upsilon)$ (it corresponds to the first vibrational level) from the data[7] is only 0.08%. And the deviations of the present results from the data[14] are also only 0.05%, 0.04%, 0.17% and 0.38% when $\upsilon = 0$, 2, 4 and 6, respectively. So it can be deduced that the vibrational levels of $^{12}C_2(X^1\Sigma_g^+)$ species given in Table 3 are accurate, though no experimental or theoretical results can be presented for comparison with them for higher vibrational levels.

There are two groups of experimental data[8,14] involving the B_υ and D_υ for the $^{12}C_2(X^1\Sigma_g^+)$ species. Excellent agreement can also be found between the present results and these data.[8,14] For example, for the present B_υ, the deviations from the experimental data[8] are only 0.46%, 0.40% and 0.28% when $\upsilon =$ 0, 2 and 4; and the deviations from the experimental data[14] are also only 0.47%, 0.40%, 0.28% and 0.00% when $\upsilon = 0$, 2, 4 and 6, respectively. For the D_υ, as a whole, excellent agreement still exists between the present values and the experimental data,[8,14] though a few D_υ values greatly deviate from them.

Only one theoretical study[2] reported the B_υ and D_υ for the $^{12}C_2(X^1\Sigma_g^+)$ species, which we do not present in Table 3 due to the page limit. By comparison with the available data,[8,14] it is easy to find that our results are obviously superior to those theoretical ones.[2]

Table 3. The present $G(\upsilon)$, B_υ and D_υ results for the $^{12}C_2$ $(X^1\Sigma_g^+)$ species when $J = 0$ and some experimental data in literature.

υ	$G(\upsilon)/\mathrm{cm}^{-1}$			$B_\upsilon/\mathrm{cm}^{-1}$			$10^6 D_\upsilon/\mathrm{cm}^{-1}$		
	this work	exp.[7]	exp.[14]	this work	exp.[14]	exp.[8]	this work	exp.[14]	exp.[8]
0	923.54	924.3	923.98	1.80259	1.81107	1.8109	6.91951	7.00315	6.97
1	2751.27	2752	2751.47	1.78497	1.79288	1.7927	6.94992	7.05398	7.02
2	4552.58	4551	4550.67	1.76719	1.77434	1.7742	6.98653	7.0944	7.11
3	6327.01		6320.67	1.74920	1.75540	1.7553	7.02618	7.2066	7.18
4	8074.20		8060.33	1.73101	1.73590	1.7359	7.06686	7.2941	7.34
5	9793.85		9768.10	1.71260	1.71570		7.12356	7.499	
6	11485.32		11441.93	1.69383	1.69381		7.19858	4.73	
7	13147.73			1.67471			7.25838		
8	14780.72			1.65552			7.29416		
9	16384.64			1.63616			7.44583		
10	17957.83			1.61552			7.80294		
11	19495.60			1.59308			7.96845		
12	20996.39			1.57126			7.71541		
13	22464.74			1.54935			10.1181		
14	23871.42			1.49455			34.3287		
15	24981.61			1.27680			23.6762		
16	25851.01			1.35898			27.5803		
17	27038.20			1.41288			18.9101		
18	28171.83			1.33389			12.5774		
19	29219.88			1.32493			3.24216		

Table 4. The present $G(v)$, B_v and D_v results when $J = 0$ for the ground-state $^{12}C^{13}C$ and $^{13}C_2$ isotopologues and experimental data for comparison.

v	$^{12}C^{13}C$				$^{13}C_2$				
	$G(v)/cm^{-1}$	B_v/cm^{-1}		$10^6 D_v/cm^{-1}$	$G(v)/cm^{-1}$	B_v/cm^{-1}		$10^6 D_v/cm^{-1}$	
	this work	this work	exp.[11]	this work	this work	this work	exp.[11]	this work	exp.[11]
0	905.61	1.73321	1.74141	6.39601	887.32	1.66381	1.67165	5.89309	5.978
1	2698.23	1.71660		6.42345	2644.10	1.64821		5.91774	
2	4465.46	1.69985		6.45644	4376.51	1.63245		5.94736	
3	6206.85	1.68290		6.49227	6084.12	1.61653		5.97960	
4	7922.04	1.66577		6.52854	7766.59	1.60043		6.01186	
5	9610.77	1.64844		6.57800	9423.65	1.58416		6.05474	
6	11272.47	1.63079		6.64522	11054.83	1.56760		6.11425	
7	12906.28	1.61280		6.70380	12659.29	1.55072		6.17108	
8	14511.75	1.59472		6.73237	14236.51	1.53372		6.19612	
9	16089.26	1.57656		6.83918	15786.83	1.51671		6.26727	
10	17637.78	1.55743		7.14436	17309.75	1.49901		6.51483	
11	19153.06	1.53651		7.38091	18801.66	1.47965		6.79039	
12	20632.30	1.51557		7.13062	20258.86	1.45967		6.63273	
13	22080.05	1.49612		7.99942	21684.61	1.44157		6.72287	
14	23485.98	1.46100		20.4983	23078.90	1.41734		12.6130	
15	24700.52	1.29675		50.3200	24362.21	1.31966		49.6369	
16	25529.48	1.24497		-37.9837	25246.16	1.15071		-22.5272	
17	26624.46	1.36764		9.50535	26204.22	1.30375		-3.49768	
18	27778.04	1.30511		18.1099	27360.49	1.27913		19.3588	
19	28813.89	1.27228		1.54678	28401.83	1.22330		3.79980	

Table 5. The present $G(v)$, B_v and D_v results when $J = 0$ for the $^{12}C_2(A^1\Pi_u)$ species and experimental data for comparison.

v	$G(v)/cm^{-1}$			B_v/cm^{-1}			$10^6 D_v/cm^{-1}$		
	this work	exp.[7]	exp.[14]	this work	exp.[14]	exp.[8]	this work	exp.[14]	exp.[8]
0	796.43	801.1	801.10	1.59782	1.60813	1.6077	6.48706	6.52569	6.46
1	2371.18	2385	2385.15	1.58092	1.59109	1.5912	6.50788	6.53614	6.5
2	3921.85	3945	3944.98	1.56393	1.57397	1.5742	6.53014	6.5731	6.6
3	5448.31	5481	5480.53	1.54687	1.55676	1.5566	6.55412	6.6026	6.59
4	6950.47	6992	6991.74	1.52971	1.53945	1.5392	6.58038	6.6289	6.59
5	8428.20	8479	8478.55	1.51247	1.52204	1.5217	6.60881	6.657	6.61
6	9881.38			1.49514		1.5042	6.64066		6.65
7	11309.88			1.47772		1.4866	6.67462		6.67
8	12713.58			1.46018		1.4691	6.70889		6.79
9	14092.37			1.44253			6.75093		
10	15446.11			1.42477			6.79378		
11	16774.66			1.40687			6.84159		
12	18077.86			1.38883			6.89238		
13	19355.57			1.37064			6.95112		
14	20607.60			1.35227			7.01588		
15	21833.74			1.33373			7.09070		
16	23033.76			1.31498			7.17360		
17	24207.42			1.29599			7.26857		
18	25354.40			1.27675			7.37497		
19	26474.38			1.25721			7.49726		

Table 6. The present $G(\upsilon)$, B_υ and D_υ results for the $A^1\Pi_u$ electronic state of $^{12}C^{13}C$ and $^{13}C_2$ isotopologues when $J = 0$ and some experimental data for comparison.

	$^{12}C^{13}C$				$^{13}C_2$				
υ	$G(\upsilon)/cm^{-1}$	B_υ/cm^{-1}		$10^6 D_\upsilon/cm^{-1}$	$G(\upsilon)/cm^{-1}$	B_υ/cm^{-1}		$10^6 D_\upsilon/cm^{-1}$	
	this work	this work	exp.[11]	this work	this work	this work	exp.[11]	this work	exp.[11]
0	780.97	1.53634	1.54630	5.99627	765.20	1.47484	1.48436	5.52476	5.568
1	2325.51	1.52040	1.53026	6.01510	2278.88	1.45986	1.46930	5.54173	5.636
2	3846.87	1.50439		6.03519	3770.32	1.44481		5.55979	
3	5344.97	1.48831		6.05679	5239.42	1.42968		5.57917	
4	6819.69	1.47215		6.08041	6686.06	1.41449		5.60032	
5	8270.91	1.45590		6.10588	8110.14	1.39922		5.62303	
6	9698.51	1.43958		6.13457	9511.54	1.38388		5.64879	
7	11102.38	1.42317		6.16492	10890.13	1.36846		5.67578	
8	12482.39	1.40665		6.19547	12245.82	1.35295		5.70293	
9	13838.45	1.39004		6.23306	13578.49	1.33735		5.73635	
10	15170.40	1.37332		6.27108	14888.02	1.32165		5.77001	
11	16478.13	1.35648		6.31367	16174.29	1.30585		5.80772	
12	17761.49	1.33952		6.35836	17437.16	1.28993		5.84699	
13	19020.35	1.32241		6.41009	18676.50	1.27389		5.89220	
14	20254.52	1.30515		6.46677	19892.16	1.25771		5.94175	
15	21463.83	1.28773		6.53213	21083.97	1.24139		5.99840	
16	22648.06	1.27013		6.60448	22251.73	1.22490		6.06144	
17	23806.99	1.25233		6.68676	23395.25	1.20824		6.13225	
18	24940.35	1.23429		6.77904	24514.28	1.19138		6.21207	
19	26047.84	1.21600		6.88399	25608.57	1.17429		6.30169	

With respect to the ground-states of $^{12}C^{13}C$ and $^{13}C_2$ isotopologues, only one experimental study[11] reported the B_υ and D_υ values. For the same reason as Table 3, we only gave some of them in Table 4 for comparison. Good agreement can still be found. For example, for the $^{12}C^{13}C(X^1\Sigma_g^+)$ species, the deviations of the present B_υ and D_υ from the data[11] are 0.47% and 2.05%; and for the $^{13}C_2(X^1\Sigma_g^+)$ species, the deviations from the data[11] are also only 0.47% and 1.42% when $\upsilon = 0$, respectively.

For a given electronic state such as $X^1\Sigma_g^+$, the vibrational manifolds of three isotopologues are determined by the same PEC and the same fitting approach. Therefore, according to the excellent agreement between the vibrational levels of the $^{12}C_2$ and the RKR data, we can still conclude that those of $^{12}C^{13}C$ and $^{13}C_2$ isotopologues given in Tables 4 are accurate, though no experimental data exist in the literature for the two isotopologues.

Table 5 tabulates the present $G(\upsilon)$, B_υ and D_υ results of $^{12}C_2(A^1\Pi_u)$ isotopologues for the first 20 vibrational states and the available experimental data.[7,8,14] For the $G(\upsilon)$, because the values obtained by Read *et al.*[7] are almost the same as the ones determined by Douay *et al.*,[14] here we only compare the present results with one of them. The deviations in the present results from the experimental data[14] are only 0.58%, 0.59%, 0.59% and 0.59% when υ = 0, 1, 3 and 5, respectively. For the B_υ, the experimental data reported by Ballik *et al.*[8] are also very close to those obtained by Douay *et al.*[14] The deviations in the present values from the data[14] are only 0.61%, 0.65%, 0.63%, 0.61% and 0.60% when $\upsilon = 0$, 1, 3, 5 and 7, respectively. For the small quantity D_υ, the relative differences between the present results and the data[14] are only 0.59%, 0.12%, 0.65% and 0.72% when $\upsilon = 0$, 1, 3 and 5; and the differences between the present results and the data[8] are also only 0.42%, 1.06%, 0.54%, 0.02% and 0.07% when υ = 0, 1, 3, 5 and 7, respectively. According to these, for the same reason as noted above, the present $G(\upsilon)$, B_υ and D_υ results of $^{12}C_2(A^1\Pi_u)$ species tabulated in Table 5 should be accurate, though no experimental or theoretical results can be presented for comparison for higher vibrational states.

For the $^{12}C^{13}C(A^1\Pi_u)$ and $^{13}C_2(A^1\Pi_u)$ isotopologues, only Amiot *et al.*[11] reported the values of B_υ and D_υ when $\upsilon = 0$ and 1. In order to facilitate com-

parisons with future experimental or theoretical data, the values of the present $G(\upsilon)$, B_υ and D_υ when $\upsilon \leq 19$ are given in Table 6. For the B_υ of $^{12}C^{13}C(A^1\Pi_u)$ species, the deviations in the present results from the experimental ones[11] are 0.64% and 0.64% when $\upsilon = 0$ and 1; and for the B_υ of $^{13}C_2(A^1\Pi_u)$ species, the differences between the present results and the experimental data[11] are also only 0.64% and 0.64% when $\upsilon = 0$ and 1. As for the D_υ, good agreement can still be obtained between the present results and experimental data.[11]

To our knowledge, for the vibrational levels of the $^{12}C^{13}C(A^1\Pi_u)$ and $^{13}C_2(A^1\Pi_u)$ isotopologues, no experimental or theoretical results can be found in the literature up to now. Similar to those of the $C_2(X^1\Sigma_g^+)$ radical, because the vibrational manifolds of three isotopologues are determined by the same PEC and the same fitting approach, we can also conclude that the values of $G(\upsilon)$, B_υ and D_υ tabulated in Table 6 are accurate according to the excellent agreement between those of $^{12}C_2(A^1\Pi_u)$ species and the RKR data.

4. Conclusions

In this paper, the PECs of the $X^1\Sigma_g^+$ and $A^1\Pi_u$ electronic states of the C_2 radical have been studied using the MRCI theory in combination with the correlation-consistent basis set, aug-cc-pV6Z, in the valence range for internuclear separations from 0.08 nm to 1.66 nm. For the two electronic states, the spectroscopic parameters of three isotopologues, $^{12}C_2$, $^{12}C^{13}C$ and $^{13}C_2$, have been investigated and compared with previous results reported, and excellent agreement has been found between the data presented here and the available experimental data. With the PECs of the C_2 radical obtained here, by solving the ro-vibrational Schrödinger equation using Numerov's method, the complete vibrational levels and inertial rotation and centrifugal distortion constants for the $^{12}C_2$, $^{12}C^{13}C$ and $^{13}C_2$ isotopologues have been calculated for the two electronic states when $J = 0$. The results for the first 20 vibrational levels are reported. Comparison with the available experimental data shows that the present spectroscopic parameters and molecular constants are both reliable and accurate.

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